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PREVENTION OF HEAVING IN STRUCTURES BUILT ON BLACK SHALE BY PRE--ETC(U)
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19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Gypsum; black shale heave; inhibition; crystallization

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This project investigated the effects of commercial inhibitor and other organic chemicals on the nucleation, growth rates, precipitate mineralogy, and crystal morphology of calcium sulfate minerals. The major goal of the study was to determine if black shale heave, a construction engineering problem caused by subsurface gypsum growth, might be minimized within laboratory simulations of the heave environment by crystallization inhibitor chemicals. Under acid conditions which characterize black shale heave environments, one inhibitor, diethylene triamine penta(methylene phosphonic acid) was clearly more effective than other

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commercial inhibitor substances and may be significantly effective in minimizing black shale heave.

Prevention of Heaving in Structures

Built on Black Shale by Prevention of Crystal Growth

Within the Shales

Final Report

Robert D. Cody

June 30, 1982

U. S. Army Research Office

Contract Number DAAG29-79-C-0030

Iowa State University

Earth Sciences Department

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WITHIN THE SHALES

Final Report on Army Research Office
Contract DAAG29-79-C-0030

OBJECTIVES OF THE RESEARCH PROJECT

This research project investigated the effects of commercial crystallization inhibitor chemicals and other selected organic substances on the nucleation, growth, precipitate mineralogy, and crystal morphology of calcium sulfate minerals. The primary goal of the investigation was to determine if effective crystallization inhibitors are available to reduce the nucleation and growth of gypsum, $CaSO_4.2H_2O$, within simulated black shale environments. If such inhibitors are available, black shale heave, a major contruction engineering problem at many localities, might be minimized or alleviated by injection of these chemicals into the shales beneath previously-built constructions. A second goal of the study was to obtain information about the effects of organic substances on the geochemistry of calcium sulfate minerals in order to better understand the geological significance of organic molecules, which are very common constituents of ancient evaporite bearing rocks.

METHODS OF STUDY

Two major methods were employed to determine the relative effectiveness of selected organic chemicals on the calcium sulfate - water system. A rapid test method was initially used to determine the relative effectiveness of each chemical in preventing the nucleation of gypsum under supersaturated conditions. In the tests supersaturation was achieved by rapidly adding enough $CaCl_2.2H_2O$ to a $(NH_4)_2SO_4$ solution so that precipitation of gypsum should begin within about 2½ minutes after mixing in the absence of an effective nucleation suppressant. The short term, 15 minute, room temperature, effectiveness of one part/thousand of each potential inhibitor was evaluated by comparing the time required for nucleation to occur (the induction period), I_a, in the presence of the organic additive to the induction period I_c, in the absence of additive. The time required for detectable nucleation to begin after mixing of the two solution was determined by continuous monitoring of visible light transmittance of the test solution by means of a photocell connected to a strip chart recorder. Two pH conditions, pH 2.5 and pH 5-7, were used to evaluate the effect of solution pH on inhibitor effectiveness. Results of the optical monitor experiments are given in Fig. 1a-1e.

The second test method utilized long term U-tube diffusion-controlled growth systems in which nucleation and growth of calcium sulfate minerals were induced within a bentonite clay matrix, the clay matrix containing a small amount of organic additive. In one arm of the U-shaped tube a 0.5 molar $CaCl_2.2H_2O$ solution was added above the clay gel growth matrix located at the base of the U-tube, and a 0.5 molar $(NH_4)_2S)_4$ solution was added simultaneously to the other arm of the tube. Opposed diffusion of calcium ions and sulfate ions into the clay matrix led to a gradually increasing concentration of the reactant (nutrient) ions and eventually led to mineral crystallization within the clay. Two different pH conditions, pH 2.5 and pH 5-7, were also utilized by adjusting clay gel pH with HCl at the beginning of each experiment. Almost all these experiements were performed at 60°C in order to increase diffusion, and crystal nucleation and growth. Effectiveness of each additive in suppressing nucleation and growth was determined by comparing the weight of calcium sulfate crystals obtained in the presence of an additive to that obtained under identical conditions but without added organic substance. Results of these experiments are given in Fig. 2 for pH 2.5 and in Fig. 3 for pH 5-7. A list of the additives used in both short-term and long-term experiments with their source is given in Table I.

RESULTS OF STUDY

SHORT-TERM INDUCTION PERIOD EXPERIMENTS

Under alkaline conditions a large number of organic substances increased the induction period to greater than the 15 minute experiment duration ($I_a/I_c>6.5$), and were therefore considered as effective nucleation suppressants under the test conditions. Of the 78 additives tested, 38 or about 49% proved effective. Under acid conditions, however, much different results were obtained. Only 8 of the 78 additives, or about 10% proved effective in preventing nucleation for at least 15 minutes. These acid resistant additives were Dequest 2041, Dequest 2051, Dequest 2954, Dequest 2060, Tretolite SP252, Tretolite SP260, WTC-10, and WTC-11. All belong to the polyphosphonate chemical group. In addition, one non-phosphonate, Wayhib S, a phosphate ester, proved almost as effective as several of the phosphonate additives. These results clearly indicate that pH is an exceptionally important factor in the effectiveness of commercial and non-commercial crystallization inhibitor chemicals. Protonation of the organic functional groups at low pH almost completely destroys the inhibitory properties of most of these chemicals.

LONG-TERM DIFFUSION-CONTROLLED GROWTH EXPERIMENTS

Under the experimental conditions used in these experiments additives were judged as being strongly effective in suppressing nucleation and/or growth if their presence yielded gypsum crystal weights below the lower boundary curve C (Figs. 2, 3) of the 95% confidence interval for an individual experiment with respect to the best fit control weight/time curve A, and moderately effective if their presence yielded gypsum weights falling within the 95% C. I. for the individual field but near the lower boundary curve C. Under acid pH conditions only a few additives were even moderately effective in reducing gypsum growth weights; these were Calgon 77, AMPS monomer, K-752, NA-alginate, Natrol 42, Dequest 2051, and oleic acid. Only one additive, Dequest 2060, was strongly effective. After preliminary experiments indicated that this additive appeared to be strongly effective under acid conditions, more detailed diffusion-controlled experiments were performed. Twelve indentical U-tubes containing Dequest 2060 at pH 2.5 were prepared, and duplicate experiments were ended after 37, 49, 62, 82, 100, and 200 days. The weight yield average for 2 identical experiments versus time are illustrated in Fig. 4. In experiements lasting less than 80 days, 1% of the additive at an initial pH of 2.5 significantly reduced gypsum crystal weight yield. After 80 days rapid crystallization of gypsum occurred so that by 200 days there was essentially no difference between gypsum weight produced in the presence of Dequest 2060 and that produced in the absence of the organic substance.

At pH 5-7 a much larger number of additives were moderately effective in minimizing gypsum growth, but complications developed with several additives. Temperatures of 60°C were used during most of the diffusion-controlled experiments in order to shorten the duration of each experiment. This temperature in conjunction with a few additives at high pH caused anhydrite to precipitate in place of gypsum; consequently the effectiveness of those particular organic additives in preventing gypsum growth could not be determined at 60°C because of the formation of a different mineral phase. Further work with the anhydrite-inducing additives at room temperature was begun several months ago. Lower temperatures will prevent anhydrite crystallization, and will allow an estimate of additive effectiveness in suppressing gypsum crystallization. Results are not yet available because of the very long-term experiments required at this low temperature, but will be published when obtained. Since only a few additives created this complication, and because the major goal of the research was to determine additive effectiveness under simulated black shale conditions, i.e., at low pH conditions, this complication is not detrimental to the project conclusion.

ANHYDRITE PRECIPITATION

Laboratory precipitation of anhydrite at moderate temperatures and water salinities as induced by the presence of organic substances may have significance in helping to understand ancient and modern anhydrite precipitation in natural evaporite environments. Before the present experiments, many investigators had tried unsuccessfully to precipitate anhydrite under sedimentological conditions, and this difficulty had been used by geologists as strong evidence against the possibility that anhydrite could actually precipitate as a primary phase in evaporite environments. The results obtained in the present research project suggests this older laboratory-derived evidence is not valid because natural analogues of selective gypsum-inhibiting and anhydrite-promoting organic substances may exist and facilitiate anhydrite precipitation in nature. Early results on anhydrite precipitation obtained in this project are summarized by Cody and Hull (1980). A variety of further experiments on the subject are being undertaken by T. Masterson, a Master of Science student at Iowa State University, and the results are being prepared for publication. Fig. 5 summarizes the precipitation field for gypsum and anhydrite in the presence of polyacrylic acid as functions of water temperatures and sodium chloride water salinity, and is representative of the work continuing here.

GYPSUM CRYSTAL MORPHOLOGIES

A last aspect of the current research project was to investigage the effects of soluble organic material on the crystal morphology of gypsum produced during diffusion-controlled growth experiments. These organic additives were observed to have major effects on gypsum morphology because of the properties that cause many of the additives to suppress gypsum nucleation and growth. It is generally agreed that effective crystallization inhibitors act by being adsorbed on pre-critical nuclei of precipitating solids and thereby effectively blocking further growth on these nuclei. Because critical size is never attained these nuclei subsequently redissolve. When strongly adsorbed organic substances are present in amounts too small to completely prevent growth, their adsorption radically affects the growth morphology because of selective adsorption on certain crystal faces but not on others. Growth of the adsorbing faces is there slowed so that other faces grow in their places. Another effect of organic macromolecules in affecting growth morphologies may be due to a bridging effect were one part of a single organic macromolecule is firmly adsorbed to one growing crystal, and another part is adsorbed to a second crystal. In this way two or more growing crystals are attached to each other. If the bridging macromolecule is oriented in attaching to each crystal, then unusual and reproduceable crystal intergrowths may result.

A large number of inhibitors investigated in this project were found to produce lenticular gypsum crystals, and some of the additives lead to multiple growths, rosettes, and spherulites. In the absence of organic inhibitors, gypsum usually exhibits well-defined crystal forms $\{010\}$, $\{111\}$, $\{\bar{1}03\}$, and a prismatic habit. Very small amounts of many inhibitors such as the polyphosphonates lead to a stubby prismatic habit in which growth in the $\underline{c}$ crystallographic asix direction is reduced; larger amounts of the inhibitors drastically reduced growth along $\underline{c}$ and also lead to rounding of the corner between the crystal forms $\{111\}$ and $\{\bar{1}03\}$, thus leading to the lenticular habit so common in many naturally grown gypsum crystals. Cause of the change in morphology was found to be selective adsorption of organic substances on the (111) and ($\bar{1}$03) faces. Photographs of a few of the many distinctive crystal morphologies produced during the research project are given in Fig. 6, 7 and 8.

CONCLUSIONS

The major goal of the project was to determine if available crystallization inhibitors have the potential of reducing gypsum nucleation and growth within black shale heave environments. Such inhibitors must be effective under acid conditions and must not be adversely affected by reactions with clay minerals located within the black shales. On the basis of diffusion-controlled growth experiments together with rapid nucleation rate experiments conducted in the project, I have concluded that at least one additive satisfies these requirements in laboratory simulation of black shale heave environments. This chemical is diethylenetriamine penta(methylene phosphonic acid)*. This additive prevented crystallization of gypsum for a significant period of time at an initial pH of 2.5 and was not adversely affected by the clay growth matrix. Normally in the absence of an effective crystallization inhibitor, gypsum should nucleate and grow within approximately 20 days, whereas 1% Dequest 2060 completely prevented crystallization until 60 days (Fig. 4). Thus the additive eliminated crystallization for 40 days under exceptionally rigorous conditions. The diffusion-controlled growth systems utilized here are rigorous test systems because continued diffusion of nutrient ions in the absence of crystallization progressively increases their concentration within the bentonite gel growth matrix until the inhibition properties of almost any inhibitor will be overwhelmed by the large nutrient ion concentration. In addition, the 60°C temperatures used will increase both diffusion and nucleation-growth reactions far above those occurring at low temperatures.

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* Dequest 2060 marketed by Monsanto Corporation

Further work should be performed to more clearly define the inhibition ranges of this and other moderately effective inhibitors under a wide variety of environmental conditions, but results of the present study suggest that Dequest 2060 may have the properties required for effective minimization of gypsum growth within natural black shale environments.

TABLE I
ORGANIC ADDITIVES USED IN PROJECT

ADDITIVE	SOURCE
Amino Acetic Acid	Pfanstiehl Labs
1-Amino-2-Naphthol-4-Sulfonic-2Acid	Eastman Organic Chemicals
7 amino-1,3 Napnthaliene-Disulfonic-2-Acid	Eastman Organic Chemicals
L-Ascorbic Acid	Baker
Bactogelatin	Difco Lab
Belclene 200	CIBA-GEIGY Corp.
Belclene DP216	"
Belclene 500	"
Calgon 14	Calgon Labs
Calgon 77	"
Calgon 165	"
Calnox 214 H MW 900-1200	Magna Corp.
Catechol	Matheson Co., Inc.
Cinnamic Acid	Iowa State University Labs
D-FIOC 100H	Magna Corp.
D-FIOC 150H	Magna Corp.
Dequest 2000	Monsanto
Dequest 2010	"
Dequest 2041	"
Dequest 2051	"
Dequest 2054	"
Dequest 2060	"
3,3 dimethyl-glutaric Acid	Nutrional Biochemicals Corp.
Disodium EDTA	Iowa State University Labs
EMA 1103	Monsanto?
Ethoquad 6012909 R113-50	Armak
Ethoquad 6921305 R115-50	Armak
Gallic Acid	JT Baker
Glutamic Acid	Iowa State University Labs
Glycerol-a-p chlorophenyl ether	Pfaltz & Bauer, Inc.
Guar Gum F6 60-50	Mercules Food Gums PFW Inc.
8-Hydroxy-guinolne	JT Baker
K702	BF Goodrich
K732	"

TABLE I

ADDITIVE	SOURCE
K732 K739	BF Goodrich
K759	"
Maleic Acid	Matheson, Coleman and Bell
Methocel K15M	Dow made 11/15/79
Methyl Pyrrdidone (M-PYROL)	GAF Corp.
Mucic Acid	Matheson, Coleman and Bell
Nateol 42	Proctor Chemical Co. Inc.
Natrosol	Hercules Inc.
Nucleic Acid	Eastman Kodak Co.
Oleic Acid	Matheson, Coleman and Bell
Oxalic Acid	Iowa State University Labs
PBS.AMV/800 .4559	Mobay Chem Corp.
Phytic Acid	Iowa State University Labs
Phytol	Pfaltz & Bauer, Inc.
Polyacrylate AB-08	Calgon Corp.
Polyacrylic Acid KXP8	Goodrich
Polyhall M295	Celanese
Polyhall 650	Celanese
Polyhall 990	"
Polyfon O	Westvaco Chem Division
2-Pyrrolidone 2-Pyrol	GAF Corp
REAX 6BW	Westvaco
REAX 82	Westvaco
REAX 100	Westvaco
Sulfamic Acid	JT Baker
Tannic Acid	JT Baker
Tartaric Acid	Mallinckrodt
Tret-o-Lite SP252	Petrolite Corp. Tretrolite Div.
Tret-o-Lite SP260	Petrolite Corp. Tretrolite Div.
Tret-o-Lite 74185	"
Tret-o-Lite 74186	"
Tret-o-Lite 74187	"
Tret-o-Lite 74188	"
Tret-o-Lite 93183	"
VERSA TL3	Proctor Chem Co.
VERSA TL4	"

TABLE 1

ADDITIVE	SOURCE
WTC-04	Monsanto
WTC-05	"
WTC-06	"
WTC-10	"
WTC-11	"
WTC-13	"
Sodium Citrate	JT Baker
Sodium Alginate	Mallinckrodt
Tretolite, Ionene 93007	Petrolite Corp.
Tretolite, Ionene 93012	"
Wayhib S	Phillip A. Hunt Corp.

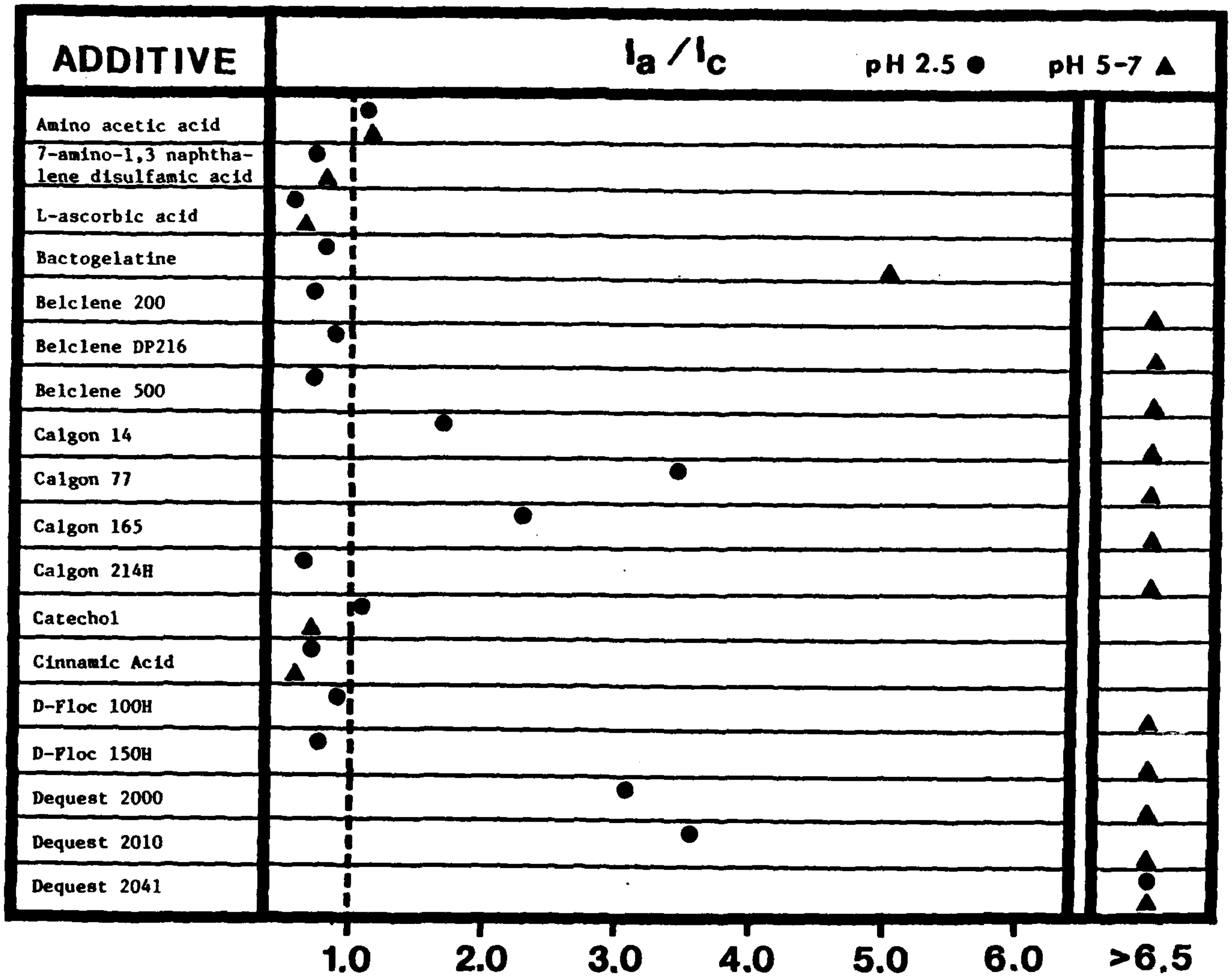


Fig. 1a. Induction period ratio for gypsum monitored by optical transmission. Ia: induction period in the presence of potential organic crystallization inhibitor. Ic: induction period in the absence of added organic chemical. Effective nucleation inhibitors will increase the time before nucleation commences after supersaturation occurs. In the present study, a ratio of Ia/Ic > 6.5 is taken as **evidence of very effective inhibition.**

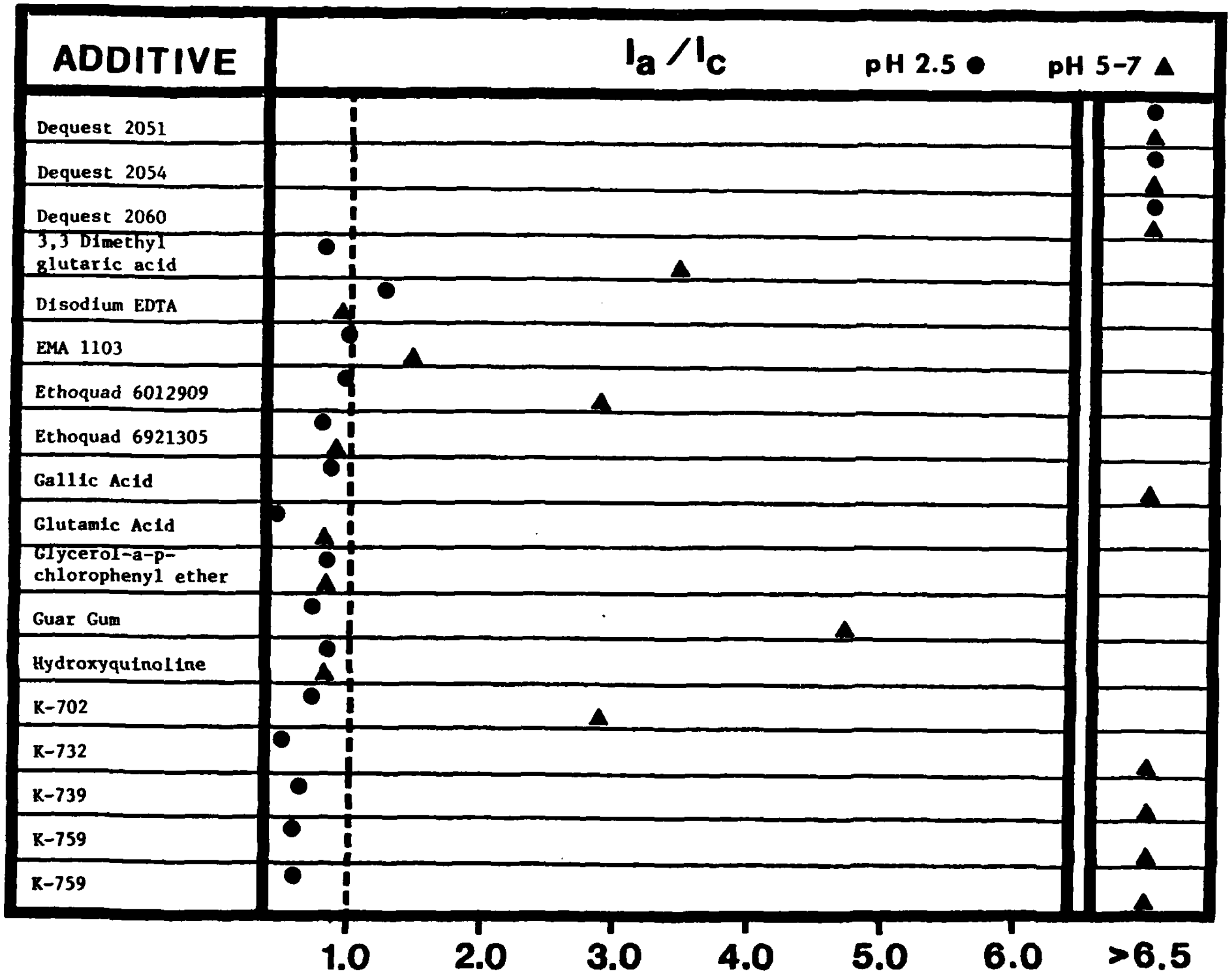


Fig. 1b. Induction period ratio for gypsum monitored by optical transmission. Ia: induction period in the presence of potential organic crystallization inhibitor. Ic: induction period in the absence of added organic chemical. Effective nucleation inhibitors will increase the time before nucleation commences after supersaturation occurs. In the present study, a ratio of Ia/Ic > 6.5 is taken as evidence of very effective inhibition.

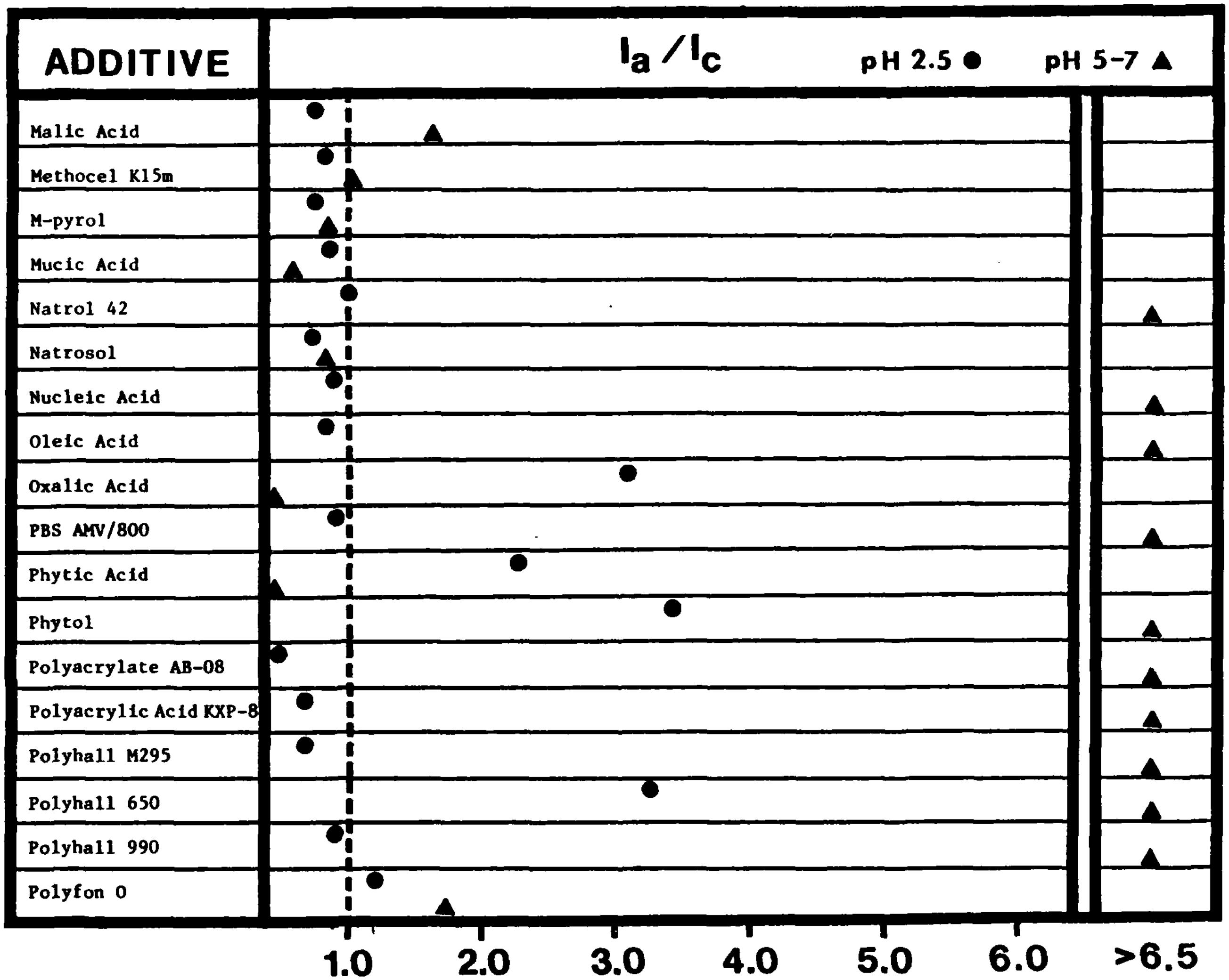


Fig. 1c. Induction period ratio for gypsum monitored by optical transmission. Ia: induction period in the presence of potential organic crystallization inhibitor. Ic: induction period in the absence of added organic chemical. Effective nucleation inhibitors will increase the time before nucleation commences after supersaturation occurs. In the present study, a ratio of Ia/Ic > 6.5 is taken as evidence of very effective inhibition.

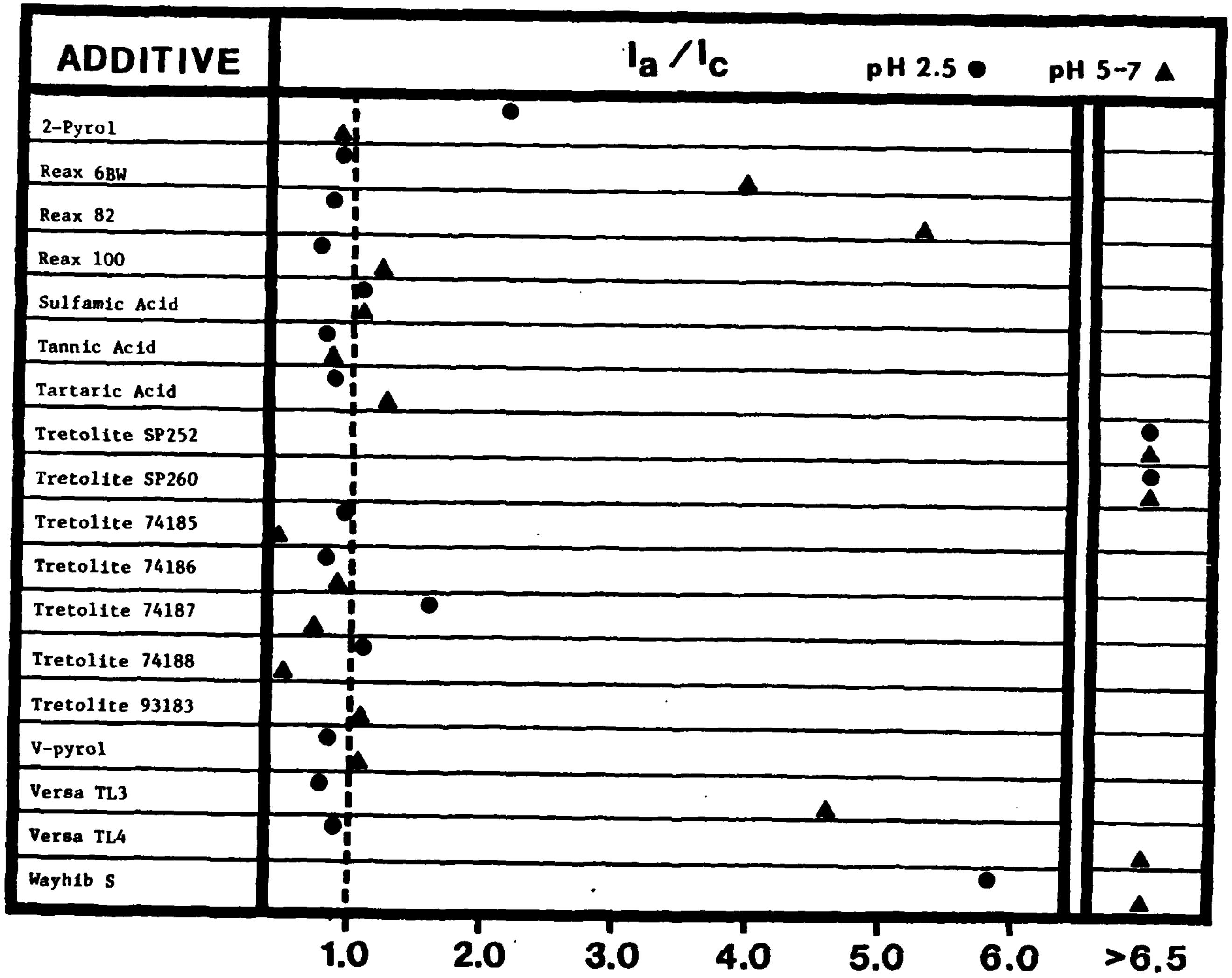


Fig. 1d. Induction period ratio for gypsum monitored by optical transmission. Ia: induction period in the presence of potential organic crystallization inhibitor. Ic: induction period in the absence of added organic chemical. Effective nucleation inhibitors will increase the time before nucleation commence after supersaturation occurs. In the present study, a ratio of Ia/Ic > 6.5 is taken as evidence of very effective inhibition.

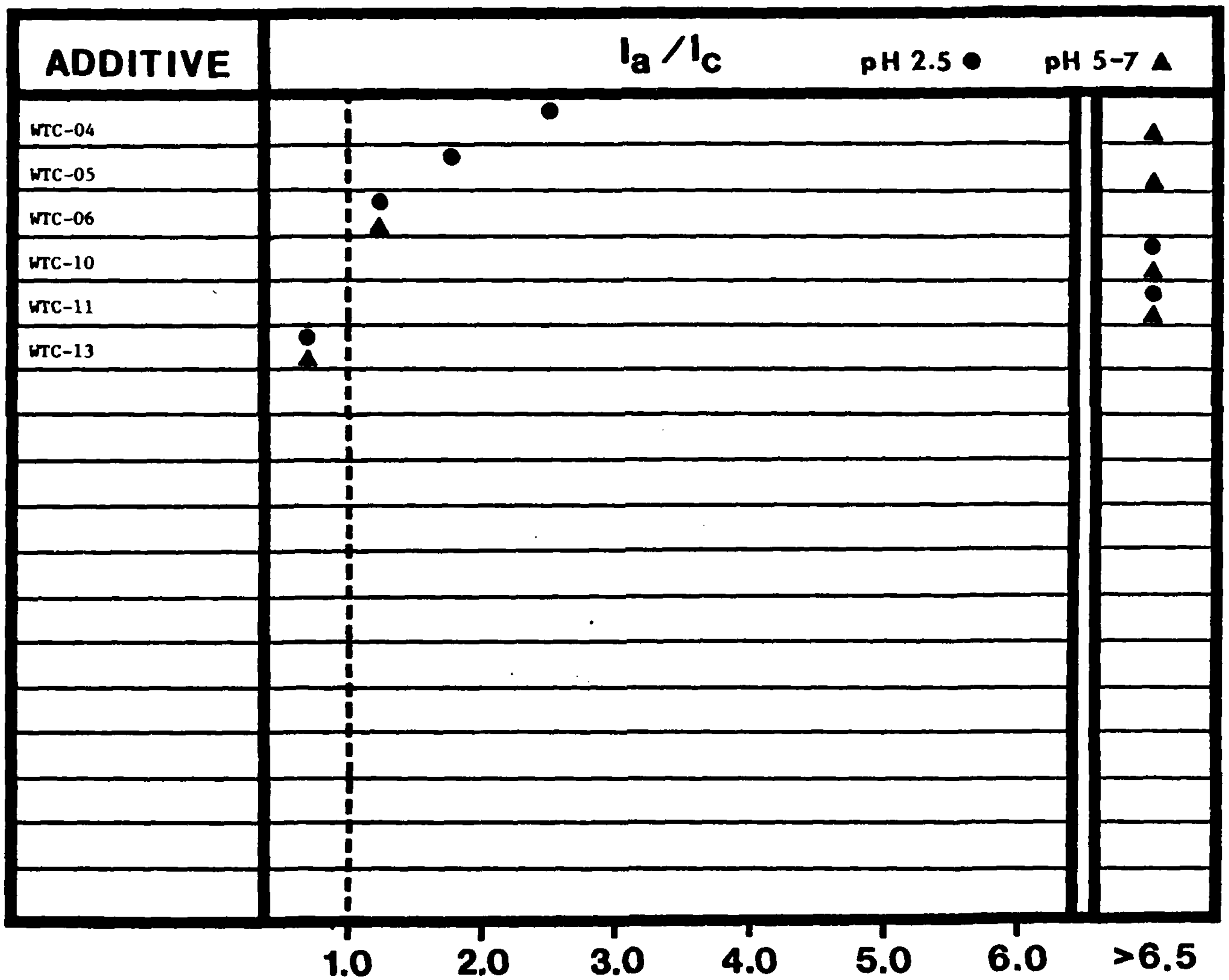
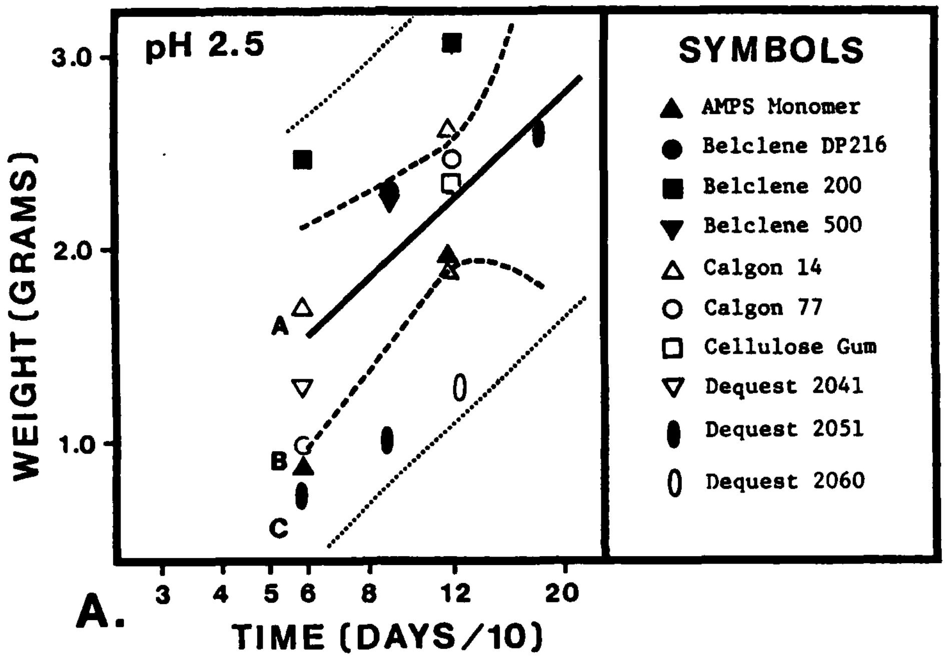


Fig. 1e. Induction period ratio for gypsum monitored by optical transmission. Ia: induction period in the presence of potential organic crystallization inhibitor. Ic: induction period in the absence of added organic chemical. Effective nucleation inhibitors will increase the time before nucleation commences after supersaturation occurs. In the present study, a ratio of Ia/Ic > 6.5 is taken as evidence of very effective inhibition.



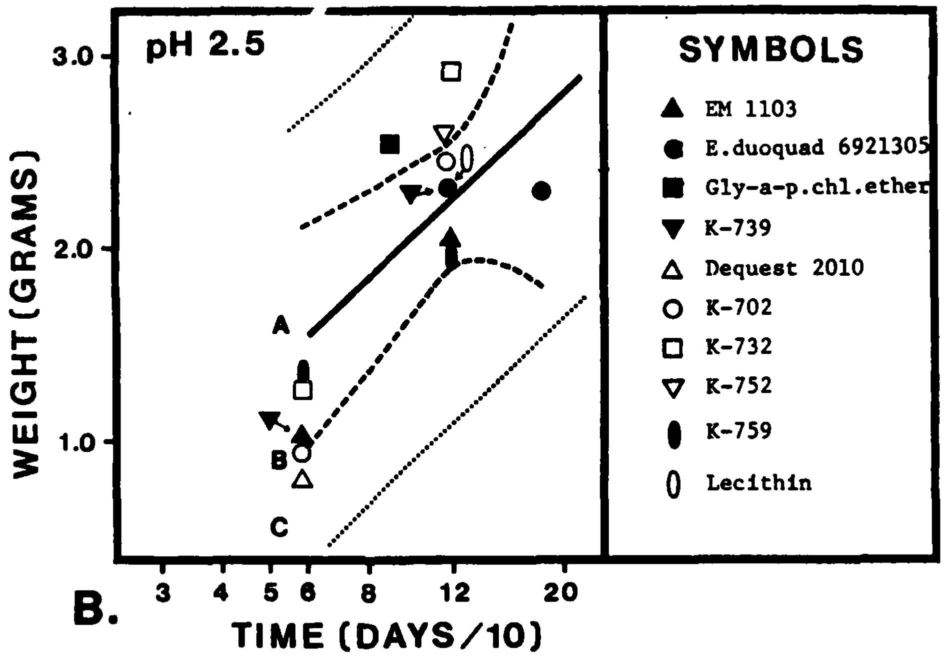
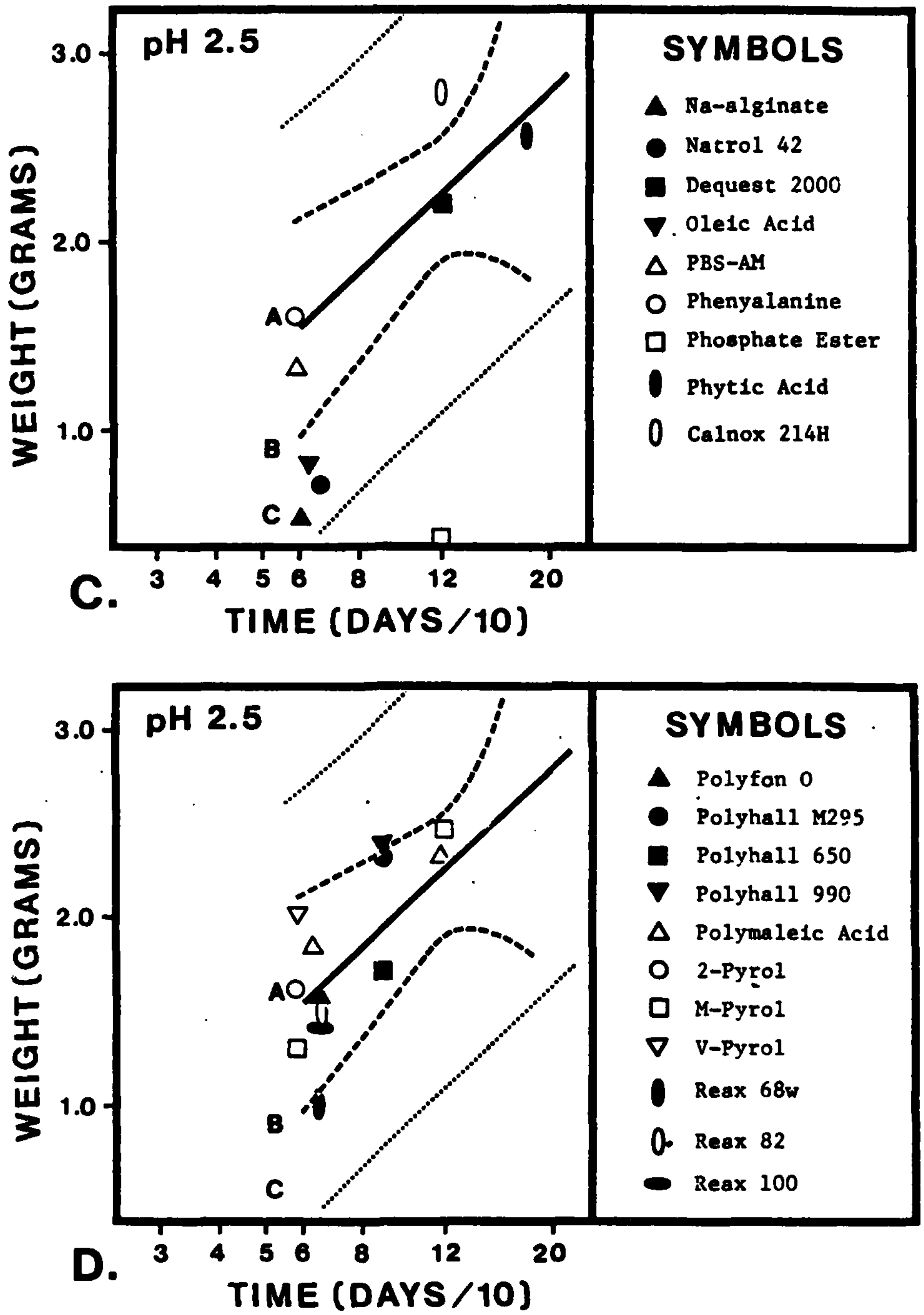


Fig. 2. Growth rates of gypsum in U-tube diffusion experiments in the presence of potential organic crystallization inhibitors. Growth matrix was bentonite clay gel; initial pH of the gel was adjusted to pH 2.5 by addition of HCl. Solid line A: best fit growth rate curve for gypsum in the absence of added organic chemicals. Dashed line B: 95% confidence interval for the mean. Dotted line C: 95% C.I. for the individual. In order to be classed as an effective inhibitor, the organic additive should reduce gypsum nucleation and/or growth rates so that its weight plots below curve C.



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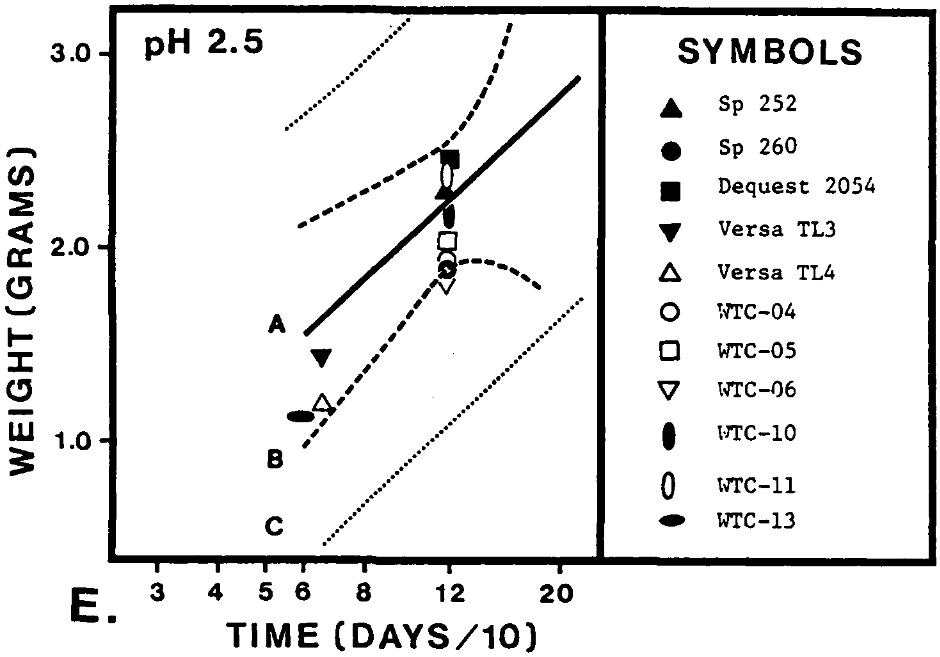

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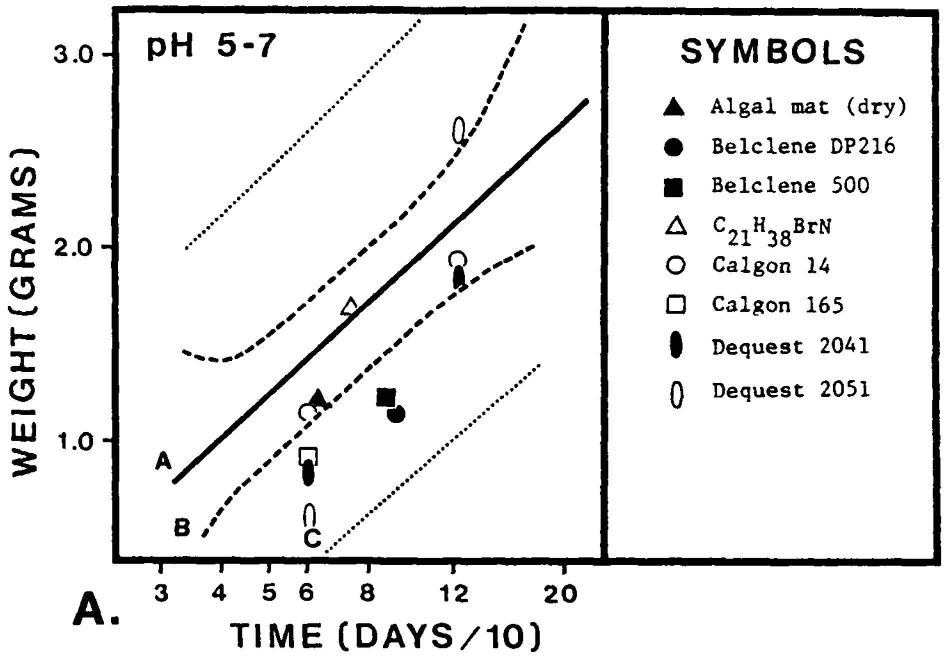


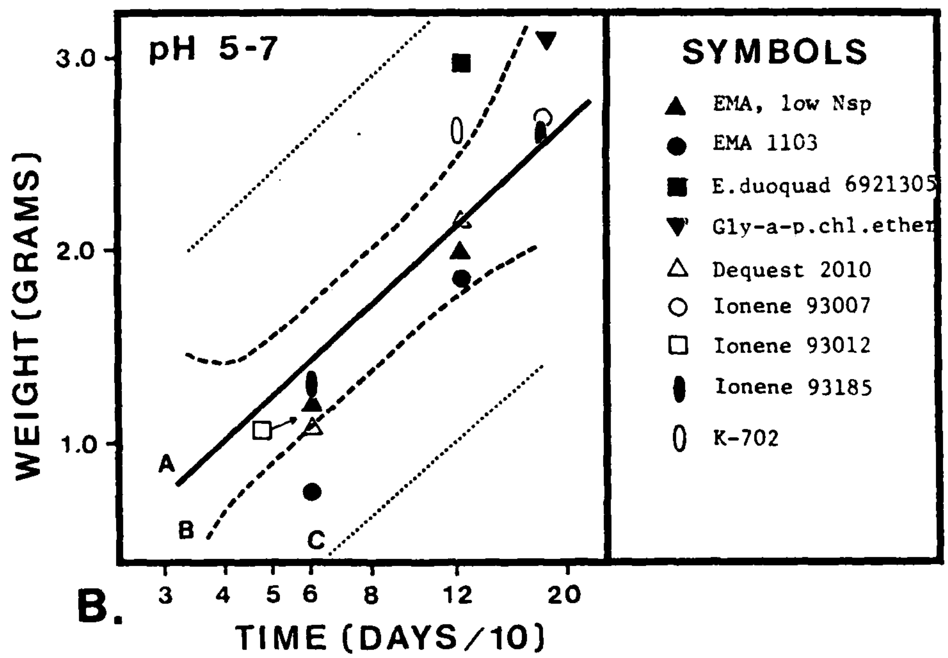
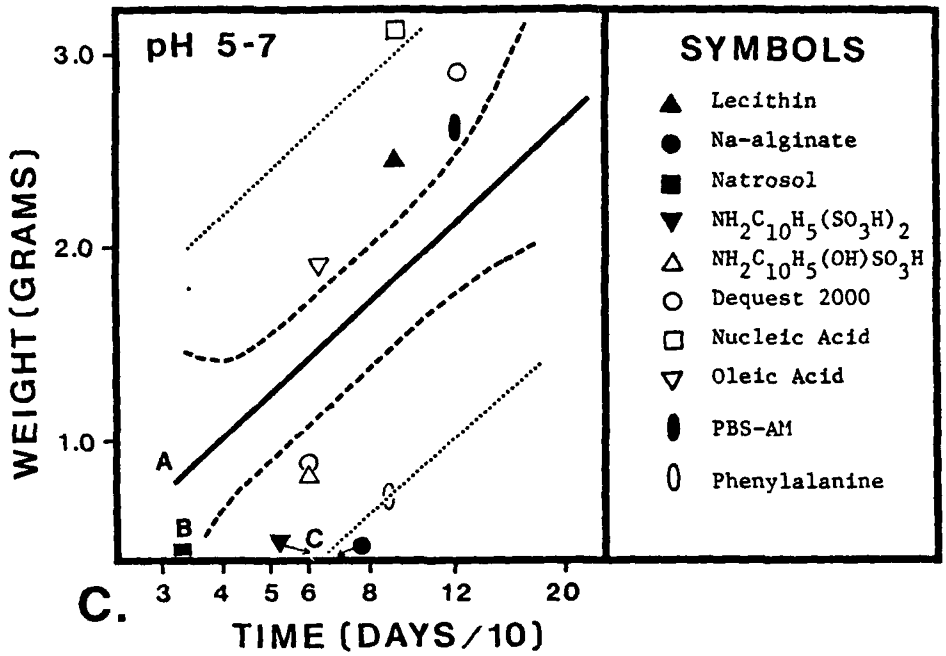


Fig. 3. Growth rates of gypsum in U-tube diffusion experiments in the presence of potential organic crystallization inhibitors. Growth matrix was bentonite clay gel; pH of the gel was not adjusted. Solid line A: best fit growth rate curve for gypsum in the absence of added organic chemicals. Dashed line B: 95% confidence interval for the mean. Dotted line C: 95% C.I. for the individual. In order to be classed as an effective inhibitor, the organic additive should reduce gypsum nucleation and/or growth rates so that its weight plots below curve C.



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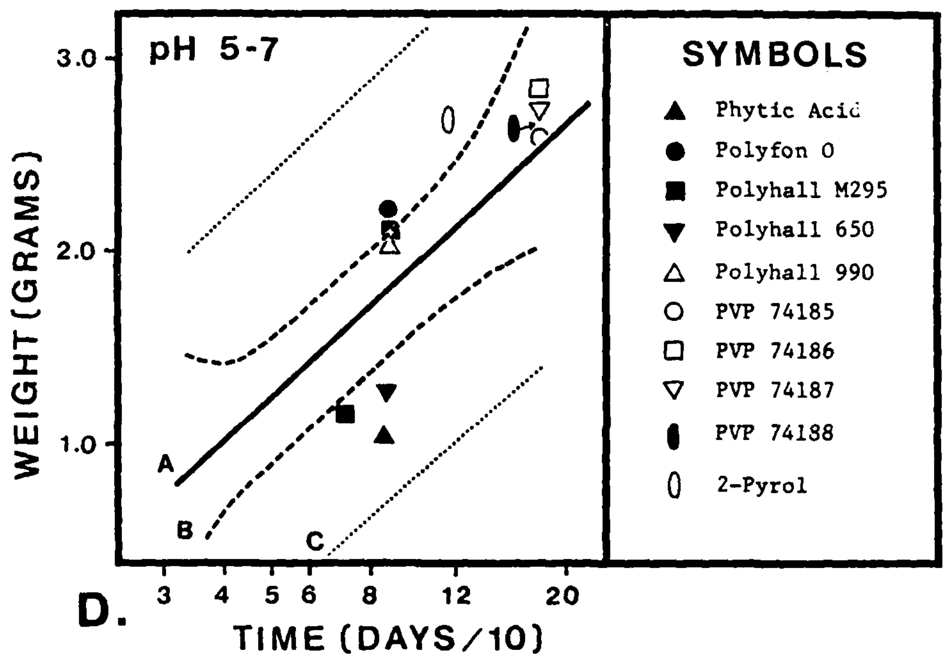

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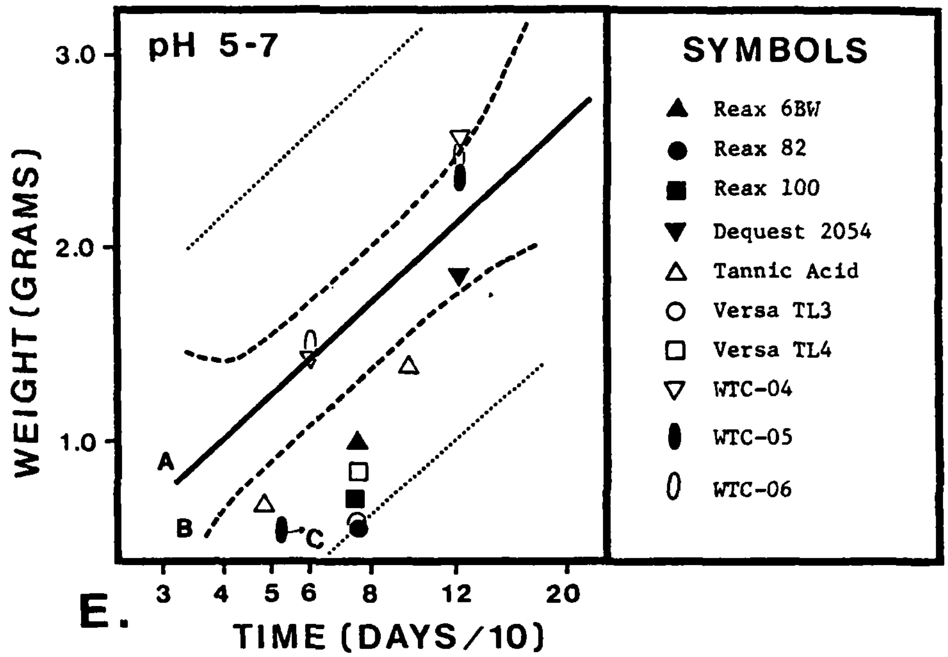
Fig. 3. Growth rates of gypsum in U-tube diffusion experiments in the presence of potential organic crystallization inhibitors. Growth matrix was bentonite clay gel; pH of the gel was not adjusted. Solid line A: best fit growth rate curve for gypsum in the absence of added organic chemicals. Dashed line B: 95% confidence interval for the mean. Dotted line C: 95% C.I. for the individual. In order to be classed as an effective inhibitor, the organic additive should reduce gypsum nucleation and/or growth rates so that its weight plots below curve C.



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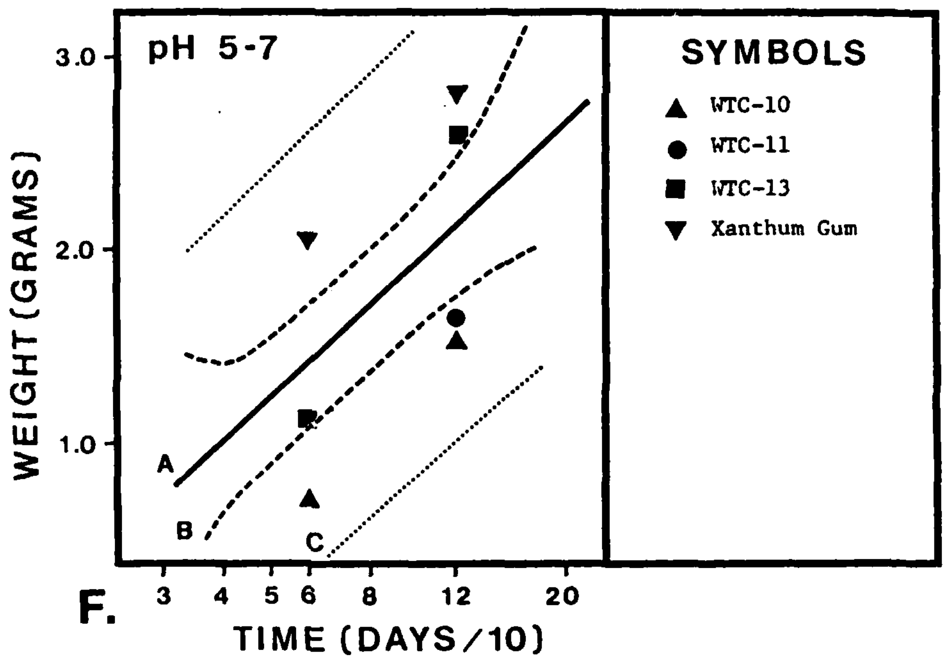

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Fig. 3. Growth rates of gypsum in U-tube diffusion experiments in the presence of potential organic crystallization inhibitors. Growth matrix was bentonite clay gel; pH of the gel was not adjusted. Solid line A: best fit growth rate curve for gypsum in the absence of added organic chemicals. Dashed line B: 95% confidence interval for the mean. Dotted line C: 95% C.I. for the individual. In order to be classed as an effective inhibitor, the organic additive should reduce gypsum nucleation and/or growth rates so that its weight plots below curve C.

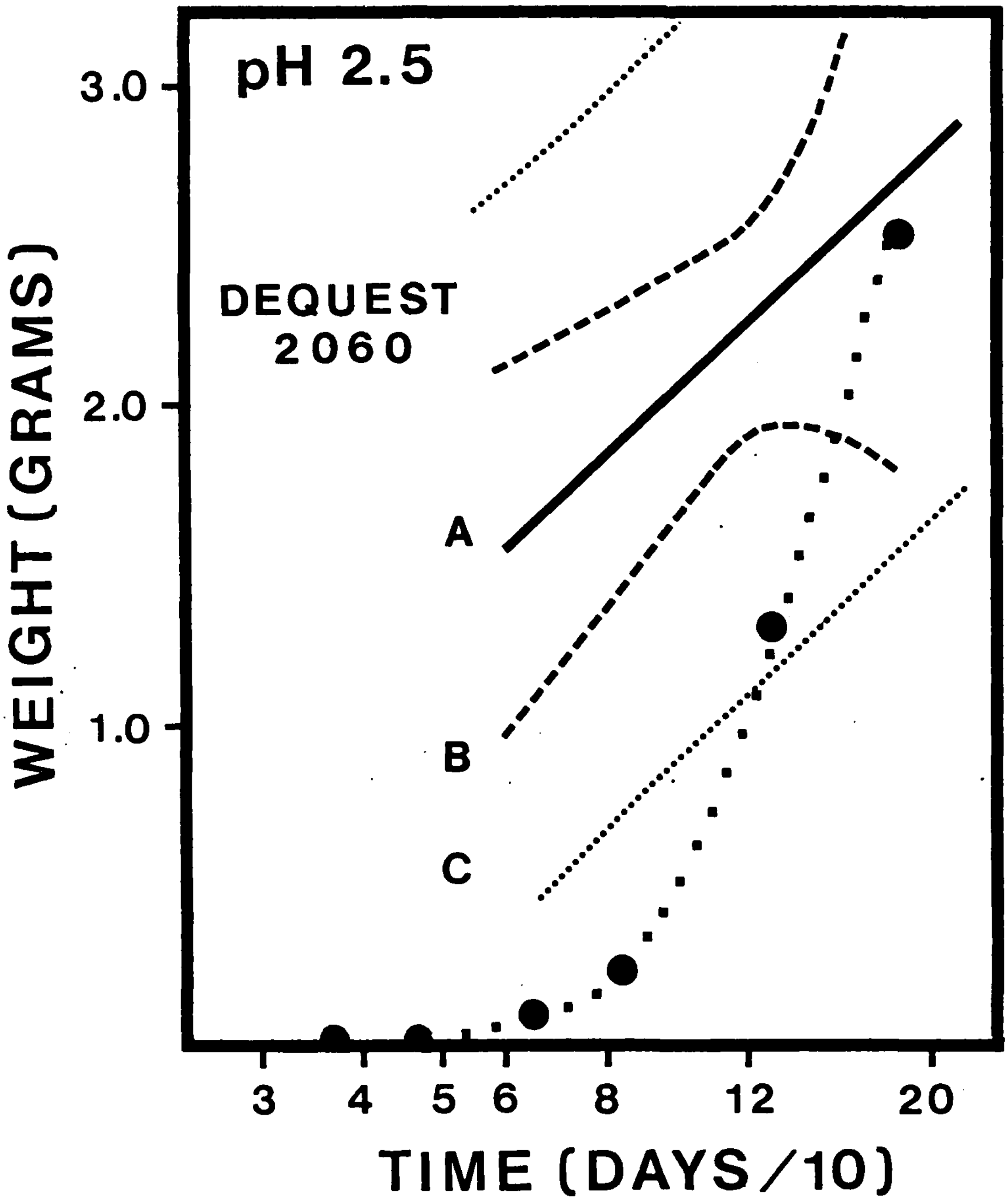

Fig. 4. Growth rate of gypsum in U-tube diffusion experiments in the presence of Dequest 2060. Growth matrix was bentonite clay gel; initial pH was approximately pH 2.5 due to the acid character of the additive. Duplicate experiments were used for each time period. Symbols are the same as in Figs. 2 and 3. Dequest 2060 proved by far to be the most effective inhibitor under acid pH conditions.

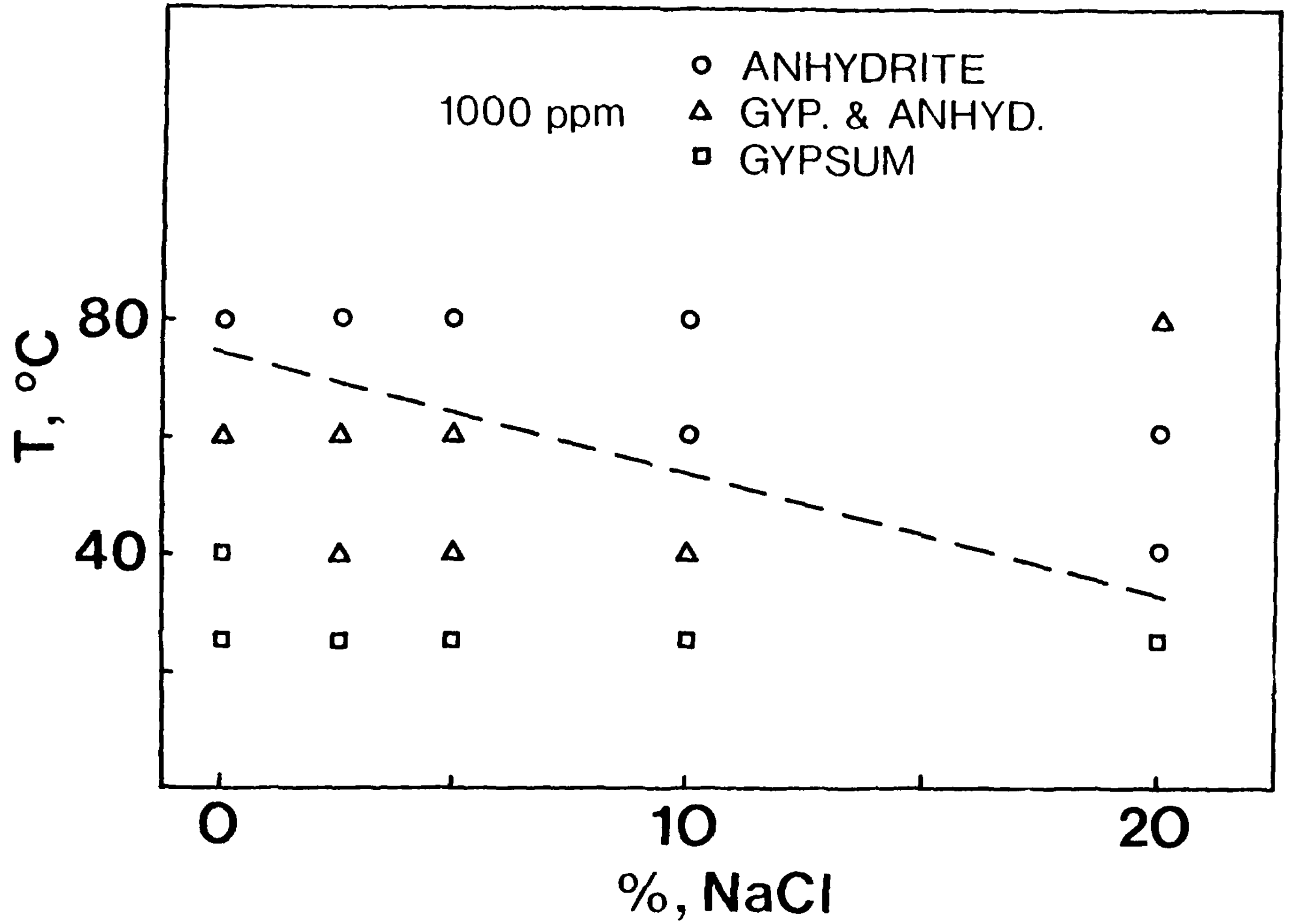

Fig. 5. Effect of salinity and temperature on gypsum-anhydrite precipitation. In these experiments 20 ml of 1/2 molar $(NH_4)_2SO_4$ containing 1 part/thousand polyacrylic acid (Calnox 214H or KXP-8) was rapidly mixed with 2 ml 1/2 molar $CaCl_2 \cdot 2H_2O$ and poured into 50 ml test tubes which were then tightly stoppered and allowed to sit undisturbed for 180 hours. The mineralogy of the precipitates was determined by x-ray powder diffraction analysis.

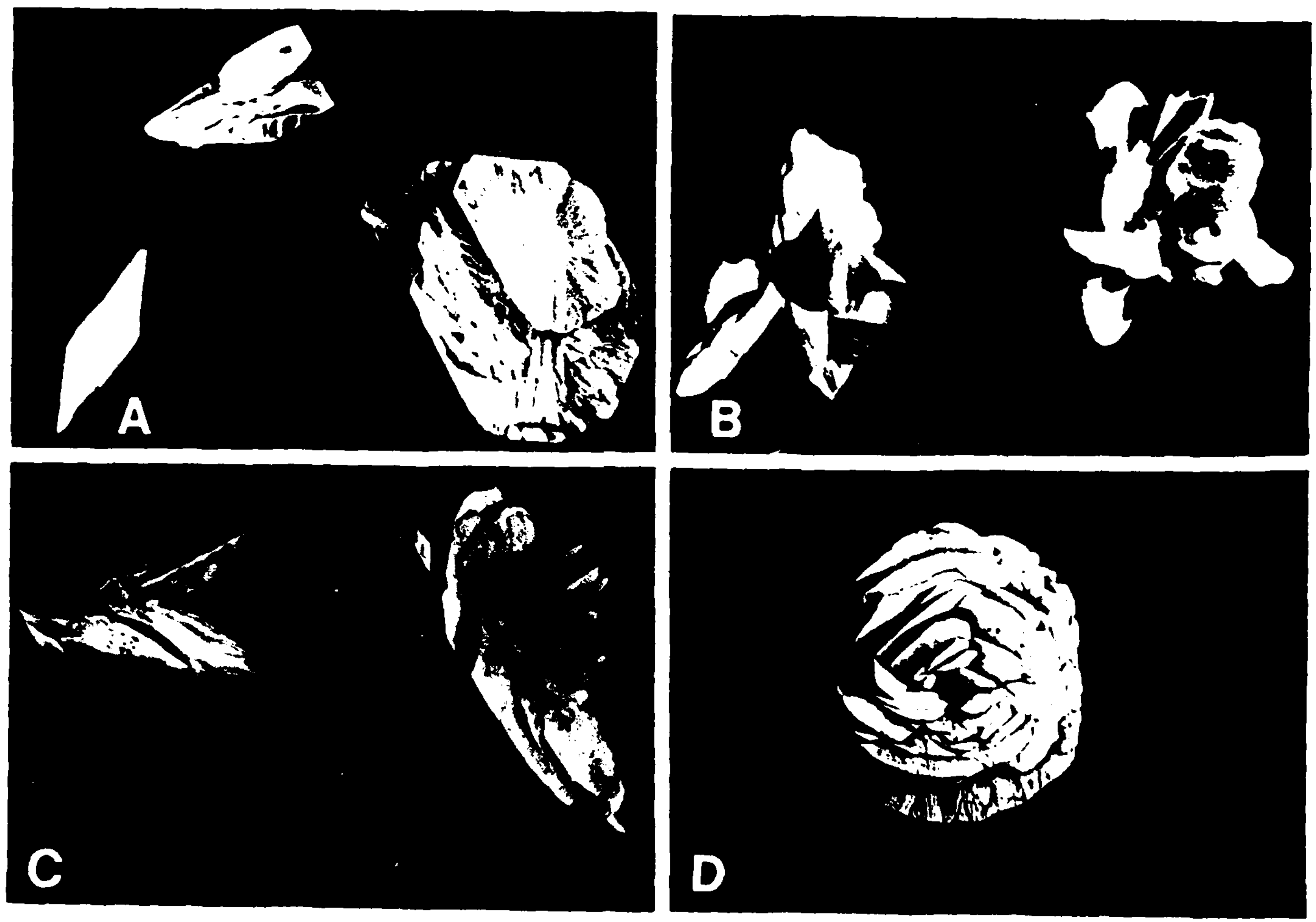

Fig. 6. Gypsum crystal morphology in presence of organic additives. All crystals were obtained in U-tube diffusion-controlled growth experiments at 60°C. Duration of growth was generally about 90-120 days. Scale is about 1:8. A. 0.01 % humic acid extracts, pH 5-7. B. 0.01% Dequest 2051, pH 5-7. C. 0.01% Dequest 2000, pH 5-7. D. 1% *tannic acid*, pH 5-7.

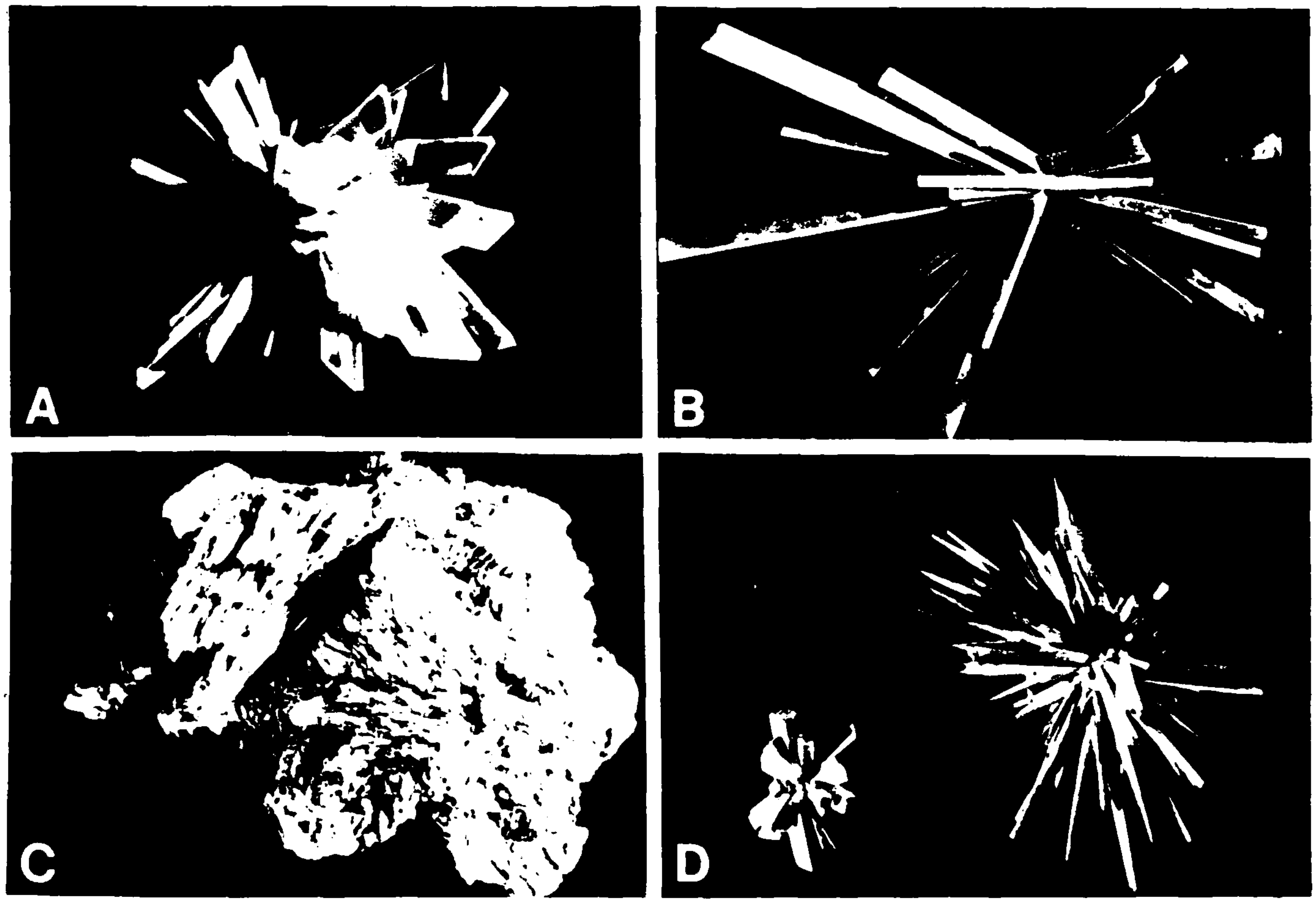

Fig. 7. Gypsum crystal morphology in presence of organic additives. All crystals were obtained in U-tube diffusion-controlled growth experiments at 60°C. Duration of growth was generally about 90-120 days. Scale is about 1:8. A. 1% Ethoduoquad 6921305, pH 2.5, 1/2% iron chloride. B. 1% lecithin, pH 2.5, 1/2% iron chloride. C. 0.1% humic acid extracts, pH 5-7. D. 1% nucleic acid, 20% NaCl, pH 5-7.

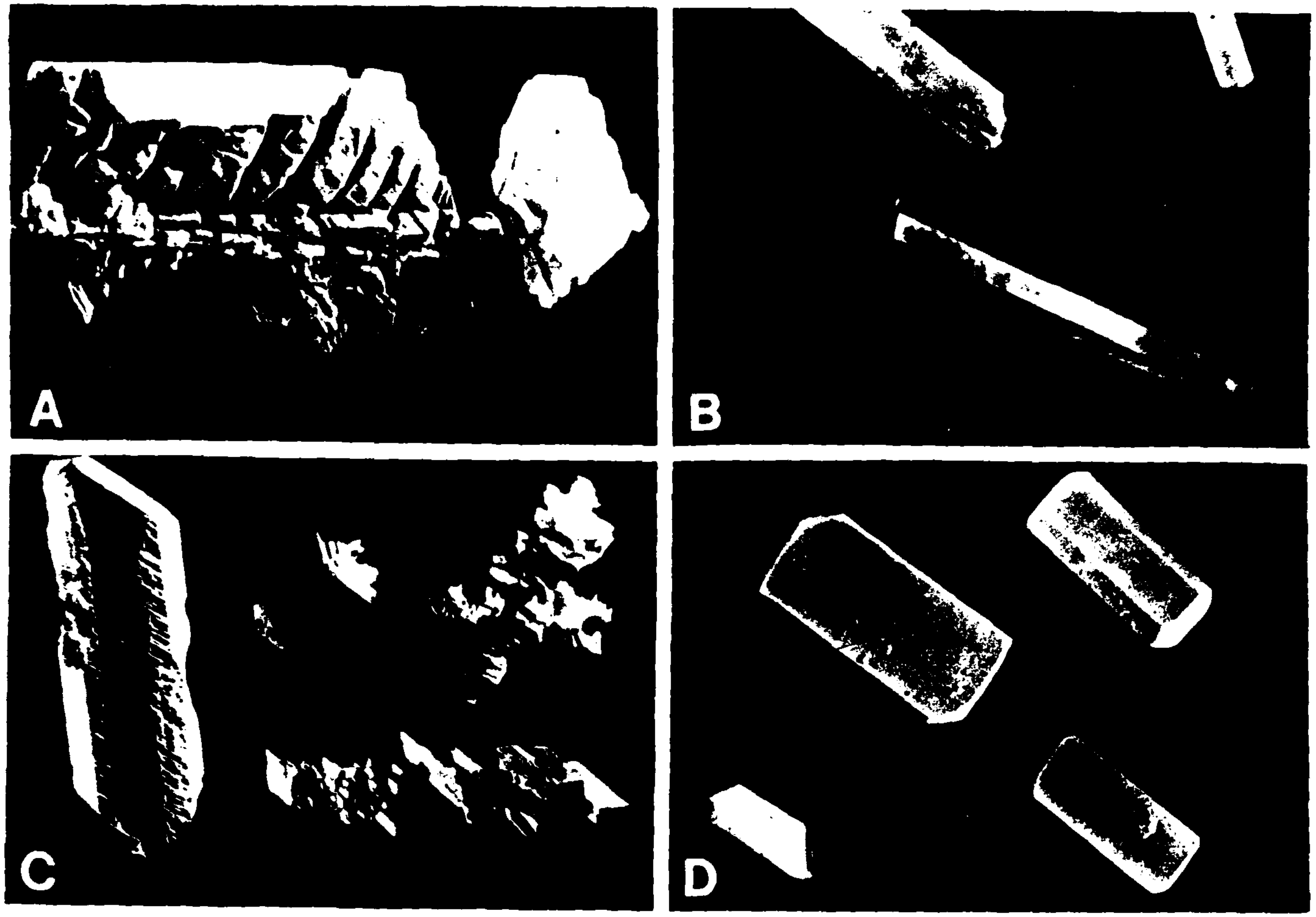

Fig. 8. Gypsum crystal morphology in presence of organic additives. All crystals were obtained in U-tube diffusion-controlled growth experiments at 60°C. Duration of growth was generally about 90-120 days. Scale is about 1:8. A. 0.01% oleic acid, pH 5-7. B. 0.01% nucleic acid, pH 5-7. C. 1% oleic acid, pH 2.5. D. 0.01% xanthum gum, pH 5-7.

PUBLICATIONS RELATED TO RESEARCH PROJECT

1. Alteration of gypsum-anhydrite precipitation kinetics by organic solutes: Iowa Academy of Science, April, 1980

2. Inhibition of gypsum-induced shale expansion; notes from a preliminary investigation on chemical modification of gypsum morphology: Geol. Soc. America, North Central Section, 14 Ann. Meeting, Bloomington, Indiana.

3. Prevention of building heave by chemical inhibiting gypsum-induced shale expansion: 21st U. S. Symposium on Rock Mechanics, Rolla, Missouri.

4. Experimental growth of primary anhydrite under sedimentological conditions: Geol. Soc. America, National Meeting, Atlanta, Georgia, Nov. 1980.

5. Scanning electron micrographic study of additive-induced morphological variations during gypsum crystallization: 17th Annual Electron Microscopy Colloquium, Ames, Iowa, May 1980.

6. Morphooogical variations of gypsum in the presence of organic macromolecules, an SEM study: Geol. Soc. America, North Central Section, 15 Ann. Meeting, Ames, Iowa.

7. Comparison of crystal morphology of synthetic and natural gypsum crystals: Geol. Soc. America, North Central Section, 15th Ann. Meeting, Ames, Iowa.

8. Experimental growth of primary anhydrite at low temperatures and water salinities: Geology, v. 8, p. 505-509.

(9) Organic threshold inhibition, a potentially important mechanism for transport and precipitation of sparingly soluble substances: submitted to Geol. Soc. America Bulletin. 26 typed pages.

PERSONNEL SUPPORTED BY CONTRACT

Period from May 1979 to January 1981

A. B. Hull, 1/2 time

Period from January 1981 to April 15, 1982

S. A. Green, 1/2 time

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